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HAZARDOUS WASTE MANAGEMENT OF METAL FINISHING WASTES

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This paper, presented at the 8th American Electroplaters' Society/Environmental Protection Agency Conference on Pollution Control for the Metal Finishing Industry, summarizes present and past metals control research conducted by EPA and presents the approach that EPA is taking to establish standards for Best Demonstrated Available Technology for hazardous wastes.

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HAZARDOUS WASTE RESEARCH PERTAINING TO METAL FINISHING

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The Environmental Protection Agency (EPA) has conducted research to evaluate or develop metal waste control techniques for a number of years. This paper presents a brief description of the more important projects that have been conducted since 1978. These projects include efforts of the programs that are conducted not only by the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory, but also those conducted by the Manufacturing and Service Industries Branch of the Water Engineering Research Laboratory. Within EPA's research program, these two Laboratories manage all of the engineering research activities of the Agency that deal with hazardous metallic wastes. During the past year, work has centered on the performance assessment of commercial facilities treating these wastes and evaluation and development of a waste reduction audit procedure.

Our preference for the management of any waste stream is represented by the following hierarchy:

- Waste elimination,
- Recycle,
- Reuse,
- Burn as fuel,
- Incineration,
- Chemical/biological detoxification,
- Volume reduction, and
- Solidify and dispose.

The performance evaluations of existing treatment technology/waste stream combinations were done to determine the best demonstrated available technology (BDAT) for that waste stream. Previously, a report[1] provided an evaluation of the sources and extent of cyanide and metal-bearing hazardous wastes and an analyses of current management practices for treating or disposing of these wastes. It includes an examination of the costs of current practices and the residuals and the emissions from treatment systems. Treatment schemes were identified which will chemically or physically treat these wastes to make them acceptable for land disposal. This information was used to develop the plan for our performance evaluation program. There are three parts to our research efforts: (1) field performance evaluations, (2) pilot tests at our Test and Evaluation Facility in Cincinnati, and

(3) examination of ways to reduce wastes. Our efforts are designed to determine acceptable ways to handle or treat wastes so that they may be land disposed.

WASTE MANAGEMENT APPROACH

The Agency's approach to managing hazardous wastes will be to require that the waste stream, after treatment, passes three tests before it may be land disposed. The first test is the "paint filter" test. This is a simple test to ensure that the waste does not contain free moisture before it is land disposed.

The Agency is considering two further tests. The first concerns the land diposal restriction, or BDAT number. For each hazardous component that may be present in a particular listed waste, EPA will establish maximum concentrations that are permissible in order for that waste to be disposed of to the land in a secure hazardous waste disposal facility. This maximum concentration will be the lowest concentration that can be achieved through treatment with the BDAT.

The other test is the proposed toxicity characteristics leaching procedure (TCLP). This is a test to determine if a waste exhibits sufficiently low toxicity that it can be disposed of to the land in a non-secure land disposal facility. This TCLP contains a health-based limit for a number of organic compounds and metals. If the leachate found through the TCLP contains concentrations of the TCLP listed compounds in excess of the limits established for the TCLP, the waste must be treated until the waste passes the TCLP.

FIELD PERFORMANCE EVALUATIONS

Field performance evaluations have been conducted for the sites listed in Table 1. The cooperation of industry with the EPA in the conduct of this performance evaluation program has been quite good. This cooperative spirit between the industry and the Government is essential in order to arrive at common-sense decisions regarding the management of these wastes. The most important findings from these tests show that there are current practices that produce a residual that contains such sufficiently high levels of organic materials that it is unable to pass the TCLP test as it is currently specified. There does not appear to be a problem in passing the EP Toxicity Test. BDAT for these wastes has not yet been codified. The Hazardous and Solid Waste Amendments of 1984 establish the statutory limits for land disposal restrictions for metal-bearing and cyanide materials that will go into effect July 7, 1987.

PLANNED PILOT-SCALE TESTS

At our Test and Evaluation Facility, we will evaluate the effectiveness of heavy metal reduction; waste concentration; removal of organic

Table 1

TEST SUMMARIES

LANDFILL BAN PERFORMANCE EVALUATION PROGRAM

SITES TESTED JUNE 1985 TO APRIL 1986

Waste Codes	Waste Composition	Waste Source	Treatment Technology
D002 Spent Nitric Acids and Metals	38% Nitric Acid (E) 5-10% Copper (E) <0.1% Organics (E) 50+% Water (E)	Electronics (Printed Circuit Board Manufacturing)	Neut./Lime Addition/ Precipitation/ Centrifugation/ Reclaimed Metal
D002, D004 Mixed Aqueous Metal-Laden	2% Arsenic (E) 25% Nitric Acid (E) 3% HF (E) 70% Water (E)	Aerospace, Auto Manufacturing	Chemical Coag./ Precipitation/ Sedimentation/ Evaporation/ Carbon Adsorption
D002, D007, F006 Waste Paint Sludge, Waste Plating Sludge, Cleaning Solution	Paint Sludge (E) Zinc Phos. Sludge (E) Biopond Sludge (E) Metal Sludge (E)	Auto Manufacturing Petroleum Air Force Base	Solidification w/Fly Ash
D002 Mixed Aqueous Metal-Laden	<5% Metals (E) <0.1% Organics (E) 95% Water (E) Trace CN (E)	Electrical Components, Applicance Manufacturing	Lime Addition/ Precipitation/ Filtration/ Carbon Adsorption
F007 Cyanide Rinse	<0.5% Metals (E) 500 ppm CN (E) 99% Water (E)	Plating	Cyanide Dest. (alkaline chlorination followed by aqueous waste treatment)

interferences, such as chelating agents, strongly complexing anions or organics which hinder heavy metal precipitation; and stabilization/solidification processes. For each system, we hope to establish the overall treatability efficiency, characterize the residuals resulting from the use of that system, and establish ways to remove interferences. The facility is designed to enable our in-house researchers to respond quickly to specific questions on waste stream treatment/technology combinations.

WASTE MINIMIZATION EFFORTS

During the past year, we have completed case studies of waste minimization programs at three plants that produce metal-laden wastes. Two of the studies were at printed circuit board manufacturers. These studies concentrated on rinse waters that follow electroplating and etching processes. The third plant manufactured mobile communication equipment components. The focus at this plant was on the second stage of a system designed to recover TCE from the first-stage stillbottoms. Reports on each of these studies are currently being prepared.

A waste reduction audit procedure has been developed and tested. It provides a methodology for identification, assessment and screening options for waste minimization. The specific objectives of our projects are:

- To generate a comprehensive list of waste minimization measures or options applicable to a specific industrial process; and
- To rank all identified waste reduction options and use these rankings to allow management to focus on options deserving further in-depth consideration.

We believe this audit procedure will help find ways to meet the RCRA requirement to certify that the volume or quantity and toxicity of hazardous wastes have been reduced to the degree economically practicable.

Several barriers that inhibit implementing waste management actions can be easily overcome by a cooperative attitude by plant management. These barriers are such things as:

- Lack of awareness;
- A "hands off the process" attitude caused by fear of upsetting a product's quality;
- Organizational inertia--"if it isn't broken, don't fix it" attitude;
- Internal politics of the organization (for example, an innovator may feel inhibited by a fear of the lack of management's support); and
- An "it can't be done" attitude; people may reject an innovative approach merely because it is outside their range of experience.

A paper by Carl Fromm and Michael Callahan discusses the audit procedure and presents a case study of its use.[2]

PAST RESEARCH PROJECTS[3]

The Environmental Protection Agency has sponsored research into metal removal and/or recovery from wastewaters and sludges for over ten years. Early efforts concentrated on precipitating metals to protect waters but the wisdom of also reclaiming metal was soon recognized as a means of reducing water pollution while conserving metal resources. Work done for EPA at Battelle Columbus in 1975 included a survey of plating facilities and the volume and types of metals discarded in sludges. As understanding of the problem began to develop, a series of investigations was funded, each adding to the overall bank of information. These projects are listed in reverse chronology below.

Metal Value Recovery from Metal Hydroxide Sludges[4]

The latest EPA projects were undertaken at the Montana College of Mineral Science and Technology (Montana Tech) and tied together much of the previous work. The first phase of the investigation was a carefully executed series of laboratory experiments to establish the processes needed to leach hydroxide sludges (the most plentiful type produced by electroplating shops) with sulfuric acid, and the various recovery methods required for copper, zinc, chromium, and nickel. Flowsheets were developed and the unit operations required to make a complete recovery process were developed.

In phase two, a pilot assembly capable of processing 75-100 lbs. of sludge per day was built and operated at a large electroplating facility. While not entirely troublefree, the operation was smooth enough to allow confirmation of the possible commercial viability of the process, and development of a computerized mass balance.

The steps of the process were as follows.

- The sludge is leached with sulfuric acid.
- Iron, which is frequently present in EP sludges, was removed by precipitating as a potassium jarosite [$KFe_3(SO_4)_2(OH)_6$]. This must be done first, as iron interferes in many of the subsequent recovery steps. This step is in need of improvement, because in the process of precipitating the jarosite some anions such as chromate are removed, along with some heavy metal cations. Even though the volume of the jarosite sludge is much less than that of the starting material, the waste would be classed as hazardous, requiring special precautions and extra costs when landfilling. Because of these faults, it is proposed that a new program be instituted to attempt to remove iron without the inclusion of large amounts of other heavy metals.

- Conventional techniques were used to extract copper from the acid solution using an oxime in petroleum solvent. The copper was then stripped from the organic phase with stronger acid and electrowon or crystallized as sulfate.

- Zinc and cadmium were extracted with diethyl hexyl phosphoric acid (D_2EHPA), leaving chromium and nickel behind. Again, a sulfuric acid strip was used for zinc removal from the organic phase. Small amounts of residual iron are removed in early stages of extraction; ten extraction stages are required to remove iron-free zinc.

- Chromium was oxidized to Cr^{+6} with chlorine, then selectively precipitated as lead chromate which can be sold as a pigment or regenerated to chromic acid with sulfuric acid. The lead sulfate precipitate formed when chromic acid is regenerated may itself be recycled to precipitate more lead chromate. In some instances SO_2/O_2 oxidation of the chromium may be more desirable.

- Nickel is precipitated as sulfide, the only heavy metal in the process which is not directly recyclable back to a plating operation. However, several alternative techniques are presented to yield a nickel ammine, or nickel sulfate may be solvent extracted with a mixture of chelating agents.

Recognizing that some improvements could be made in the various separation steps, first order cost estimates indicate that a 50-ton per day recovery plant could not only reduce landfill volume considerably, with consequent less chance of pollution, but in addition could yield a profit as shown in Table 2.

Metal Recovery from Electrochemical Machining and Electrodischarge Machining (ECM/EDM) Wastes[5]

These relatively new machining processes produce heavy metal wastes; ECM yields hydroxide sludges heavily contaminated with sodium chloride, and EDM finely divided particles of the alloy being machined. Both ECM and EDM are primarily used on hard alloys, often high in nickel, chromium, cobalt, molybdenum, etc. This project involved a survey of ECM/EDM shops, the volumes of sludge produced, metal content, and disposal practices and costs. Several recovery routes were studied, including the procedures outlined above.

Cadmium Recovery from Electroplating Wastes[6]

This project was primarily concerned with methods and costs for recovering cadmium from plating shops which are able to segregate Cd from other sludges, or perhaps those whose only business is cadmium plating. The authors give very little thought to the fact that many platers use cadmium at least occasionally, and do not segregate their sludges. The recovery technique (melt and/or distill cadmium electromotively displaced with zinc

Table 2

PROCESS COST: FIRST ORDER ESTIMATE

UNIT OPERATION	COST ($)*			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,500	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electro-winning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Chromium oxid., chromic acid production	1,818,200	503,600	407,700	911,300
6. Nickel recovery	231,600	64,200	230,000	294,200
TOTAL COST	3,868,800	1,071,900	1,362,200	2,434,100
Profit (Gross)			1,071,900	

*Assuming a $1.00 per gallon credit for sludge from producers.

metal) is most effective on low chromium and nickel sludges. While chromium is not displaced by zinc, nickel would have to be removed by distilling the zinc.

Coupled Transport Systems for Control of Heavy Metal Pollutants[7]

Coupled transport membranes are made by immersing a microporous membrane into a liquid complexing agent such as those used for liquid/liquid extraction of metals from solution. The liquid (often called a liquid ion exchanger) then acts as a transfer agent to move metal ions through the capillaries, using the driving force of the pH gradient across a membrane separating an acidic from a basic solution. Data are presented which suggest that a membrane unit having 450 to 500 square feet of surface could separate chromium from the rinse water of a medium sized plating line. The separation unit would cost about $5,000, compared to over $50,000 for an evaporative-ion exchange system.

Evaporative Recovery of Chromium Plating Rinse Waters[8]

A demonstration of this process was given by Advance Plating Company, Cleveland, Ohio on the first of four counterflow rinse tanks. After first passing through a cation exchanger to remove metallic impurities, water from the first rinse tank is drawn into a vacuum evaporator, whose condensate is returned to the third rinse tank. Concentrated acid produced in the evaporator bottoms is returned to the plating bath. The value of recovered chrome has enabled the operator to pay off the equipment in two years or less, in addition, the chromic acid in dragout water is reduced by 99.98%.

Removal of Toxic Metals from Metal Finishing Wastewater by Solvent Extraction[9]

This short investigation of solvent extraction was primarily limited to one extraction agent, Alamine 336 (General Mills). By increasing acidity stepwise with HCl, selective removal of chromium, cadmium, and zinc from wastewaters was demonstrated. Copper and nickel could not be extracted with this reagent; several other high molecular weight amines were tried without success.

Reverse Osmosis Field Test: Treatment of Watts Nickel Rinse Waters[10]

Rinse waters from a Watts type (primarily nickel sulfate) nickel plating operation were passed through a polyamide membrane, effectively separating a concentrated nickel salt solution and recycling the rinse water. Results were very encouraging, indicating that the capital cost of the R.O. unit could be recovered in about a year, based on the reduction in water usage plus metal values returned to the plating bath. This process could be more accurately described as recycling or conservation since there is no chemical change of metals recycled to the bath.

Treatment of Metal Finishing Wastes by Sulfide Precipitation[11,12,13,14]

Although the process of sulfide precipitation has been known for many years, its use as a means of pollution control appears to be of fairly recent origin, and, is mentioned here primarily to illustrate an effective method of metal removal. A major disadvantage of sulfide precipitation is the lack of selectivity; it is apparently impossible to precipitate a single metal without major contamination by other metal sulfides. Use of a polymeric flocculant (preferably anionic) increased the settling rate, and adding a chelating agent such as EDTA (ethylenediamine tetraacetic) acid at the proper pH greatly aided selectivity.

Heavy metal sulfides, even if effectively separated, are extremely difficult to reduce to their corresponding metals by hydrometallurgical methods, and are generally recovered by smelting. The large volumes of raw material required to support such smelters makes plating waste metal recovery by this method impractical.

A Reclamation of Metal Values from Metal Finishing Waste Treatment Sludges[15]

A survey of plating opertions involving over 600 questionnaires (150 replies) revealed the extent of sludges generated by the industry, and even developed a "typical" analysis of metal content; the copper, nickel, and chromium contents were very similar to those found in subsequent studies. Some preliminary laboratory leaching and extraction studies led to the conclusion that metal recovery could be economically feasible only if the process could be carried out on a large, and preferably continuous scale. Based on then current (1971) metal prices, it was concluded that chromium and zinc recovery were uneconomic; the writers apparently did not foresee the ban on landfilling of heavy metal wastes now being implemented.[12] The only laboratory work done by these investigators was leaching experiments with ammonium carbonate and sulfuric acid which indicated that acid leaches were adequate for most hydroxide sludges while ammonium carbonate would only dissolve copper and nickel. A literature study of several potential recovery methods for copper and nickel was made, but no work was done to verify their efficacy; again, chromium recovery was not considered.

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